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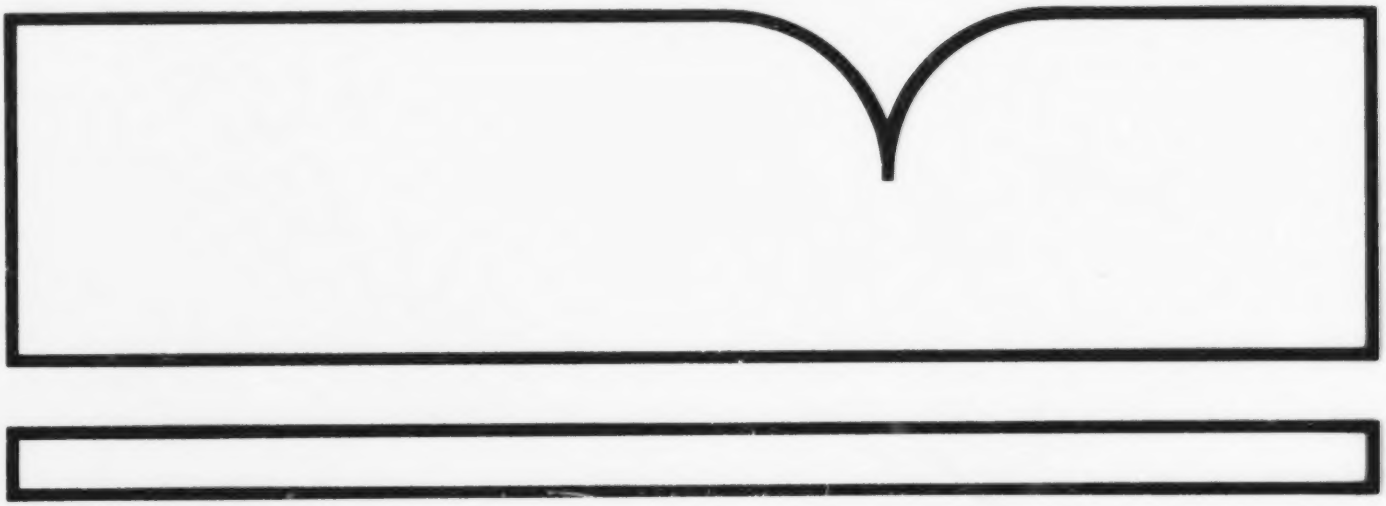

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Control of SO_x Emissions by In-Furnace Sorbent Injection: Carbonates vs Hydrates

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16. ABSTRACT The paper provides high-temperature isothermal data on SO2 capture by calcium-based sorbents, obtained in a dispersed-phase reactor for limestones, dolomites, hydrated calcitic limes, and hydrated dolomitic limes as a function of Ca/S molar ratio, temperature, and SO2 partial pressure. The experimental results indicate that SO2 capture is approximately linearly dependent on Ca/S molar ratio and relatively insensitive to SO2 partial pressure above 2000 ppm. SO2 capture is a strong function of general sorbent class; dolomitic sorbents are better than calcitic materials on an equivalent calcium basis, and hydrated materials are more reactive than carbonates. Computer model predictions based on a grain formulation, available fundamental rate data, and measured surface areas accurately predict limestone performance; however, predicted capture for the hydrated sorbents is significantly below that measured experimentally. The measured capture results do, however, generally correlate with the BET surface areas measured when the sorbents were calcined in a muffle furnace at 980 K for 20 minutes with an inert environment.

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ABSTRACT

High temperature, isothermal data on SO_2 capture by calcium based sorbents were obtained in a dispersed-phase reactor for limestones, dolomites, hydrated calcitic limes, and hydrated dolomitic limes as a function of Ca/S molar ratio, temperature, and SO_2 partial pressure. The experimental results indicate that SO_2 capture is approximately linearly dependent on Ca/S molar ratio and relatively insensitive to SO_2 partial pressure above 2000 ppm. SO_2 capture is a strong function of general sorbent class; dolomitic sorbents are better than calcitic materials on an equivalent calcium basis and hydrated materials are more reactive than carbonates. Computer model predictions based on a grain formulation, available fundamental rate data, and measured surface areas accurately predict limestone performance; however, predicted capture for the hydrated sorbents is significantly below that measured experimentally. The measured capture results do, however, generally correlate with the BET surface areas measured when the sorbents were calcined in a muffle furnace at 980 K for 20 minutes with an inert environment.

INTRODUCTION

The emission of sulfur oxides (SO_x) from the combustion of high sulfur coals in industrial boilers and furnaces is generally accepted as a major contributor to acid rain. There is, consequently, considerable interest in the development of low cost SO_2 control technologies: one such technology involves the injection of dry calcium-based sorbents into existing, coal-fired power plants. Under certain combustion conditions these sorbents (usually limestones or hydrated limes) can achieve SO_2 control by forming solid calcium sulfate which is collected at the furnace outlet. The primary advantages of pulverized, dry sorbent addition over conventional wet scrubbing for SO_2 control are its lower cost, the ease with which it can be retrofitted into existing boilers, the attractiveness of a dry product, and the reduced space requirement. The sorbents which are currently being considered for the dry sorbent injection process include limestone ($CaCO_3$), dolomite ($CaCO_3.MgCO_3$), hydrated limes ($Ca(OH)_2$), and hydrated dolomitic limes ($Ca(OH)_2.Mg(OH)_2$).

When pulverized limestone is injected into a high temperature environment it rapidly calcines to form calcium oxide:

$$CaCO_3 = CaO + CO_2.$$

At temperatures above approximately 1000 K the CaO will react with

the sulfur dioxide to produce calcium sulfate:

$$CaO + \tfrac{1}{2}O_2 + SO_2 = CaSO_4.$$

At lower temperatures $CaSO_3$ may also be a product.

BACKGROUND

Direct limestone injection for control of SO_2 emissions was the object of a research program launched by the United States Public Health Service (an EPA predecessor) in 1964. Since that time numerous fundamental, pilot scale, and full scale tests have been performed. The fundamentals of the process are now partially understood. Under oxidizing conditions the heterogeneous sulfation reaction is the result of a four step process:

- o Diffusion of the gaseous reactants to the particle surface;
- o Diffusion through the pores to the particle's interior;
- o Diffusion through the calcium sulfate product layer; and
- o Reaction at the product/reactant interface.

Earlier work by Borgwardt[1], Ishihara[2], and Howard et al.[3] indicated that the diffusion of SO_2 to the particle surface offers little resistance to the reaction if the particle diameter is less than about 50μm. The importance of pore diffusion also depends on the overall particle diameter. Hartman and Coughlin[4] concluded that the overall rate was controlled by diffusion for relatively large particles (c.a. 0.01 cm) at fairly low temperatures (823 to

1223 K). Recent results obtained by Borgwardt[5] with 1μm particles suggest that in this case the pore diffusion resistance is unimportant. With the small particles, Borgwardt found the product layer resistance to be controlling under essentially all conditions investigated. He also found a strong dependence of the reaction rate on the initial sorbent surface area, suggesting that the calcination process was of major importance in the overall reactivity of the sorbent.

The pilot and full scale testing has emphasized the practical application of the process. Coutant et al.[6] used a natural-gas-fired, dispersed-phase reactor to study the sulfation reaction with 90μm limestone and dolomite particles. They found:

- o A maximum CaO utilization of 35% for dolomite and 19% for limestones;
- o A maximum in SO_2 capture occurring at a mean gas temperature of 1311 to 1367 K;
- o That the extent of CaO utilization increased with increasing excess air; and
- o That precalcination of the limestone before injection resulted in lower CaO utilization.

Attig and Sedor[7] performed pilot scale tests using pulverized coal and obtained similar CaO utilizations. Womble et al.[8] evaluated

direct limestone injection in a full scale boiler at TVA's Shawnee Power Plant. They measured CaO utilizations ranging from 7 to 18% in this boiler with a residence time of 1.5 sec and an SO_2 concentration of approximately 3000 ppm.

Recent fundamental and pilot scale results are in general agreement with the early data regarding limestone utilization under realistic boiler conditions. Overmoe et al.[9] measured calcium utilizations from 10 to 20% with realistic thermal profiles for limestone injection. Their results indicated that the best sorbent utilizations were achieved when the sorbent was injected slightly downstream of the primary combustion zone at a temperature of approximately 1500 K. They also found that hydrated limes and dolomitic materials gave significantly higher SO_2 capture on an equivalent calcium basis. Similar results were reported by Bortz and Flament[10] and Beittel et al.[11] Recent bench scale results by Slaughter et al.[12] suggest that part of the increased reactivity associated with the dolomitic carbonates relative to the calcitic carbonates can be attributed to the development of higher surface areas during the calcination process.

Thus, the available information suggests that, for dry sorbent injection to be successful under practical, retrofit combustion conditions, sorbents other than limestones must be considered. A recent economic analysis by Lachapelle[13] suggests that dry

sorbent injection appears attractive relative to wet scrubbing in many cases, but the overall economics depends on the particular application and sorbent.

SCOPE

The overall goal of this study was to provide part of the understanding necessary to answer four practical questions related to commercial application of the sorbent injection process:

- Does hydration enhance sorbent reactivity?
- Do commercially available hydrates exhibit wide variations in reactivity?
- Will variations in coal sulfur influence sorbent utilization efficiency?
- What is the optimum location (temperature) for sorbent injection in a particular boiler?

To obtain the required high temperature sulfur capture data, a wide spectrum of calcium-based sorbents were screened under conditions where the thermal environment and sorbent properties were well characterized. A 65 kW refractory-walled reactor was used to obtain isothermal capture data as a function of calcium to sulfur ratio, SO_2 concentration, and temperature. Sorbents from each of the four major sorbent classes (limestones, dolomites, hydrated calcitic limes, and hydrated dolomitic limes) were considered.

The experimental capture data from the dispersed reactor were compared to a grain model of the sulfation process which included consideration of pore diffusion, product layer diffusion, and heterogeneous chemical reaction. Sorbent surface areas were specified as inputs based on experimental surface area measurements without SO_2 present.

In an attempt to better understand the calcination process itself, static calcination experiments were also performed in a nitrogen environment.

EXPERIMENTAL SYSTEMS

The sulfation results were obtained using the 2.5 m by 15.9 cm diameter refractory-walled furnace illustrated in Figure 1. A natural gas burner was fired at the bottom of the furnace to provide an environment of combustion products in which to characterize the sulfation reaction. The vertical portion of the furnace is an isothermal "reaction zone" which was maintained at a specified constant temperature by downfiring two 30 kW natural gas auxiliary burners through annular channels around the main combustion chamber. The reaction zone temperature was characterized with suction pyrometers containing Pt/Pt-Rh thermocouples located at the inlet and outlet of the vertical zone. Typical

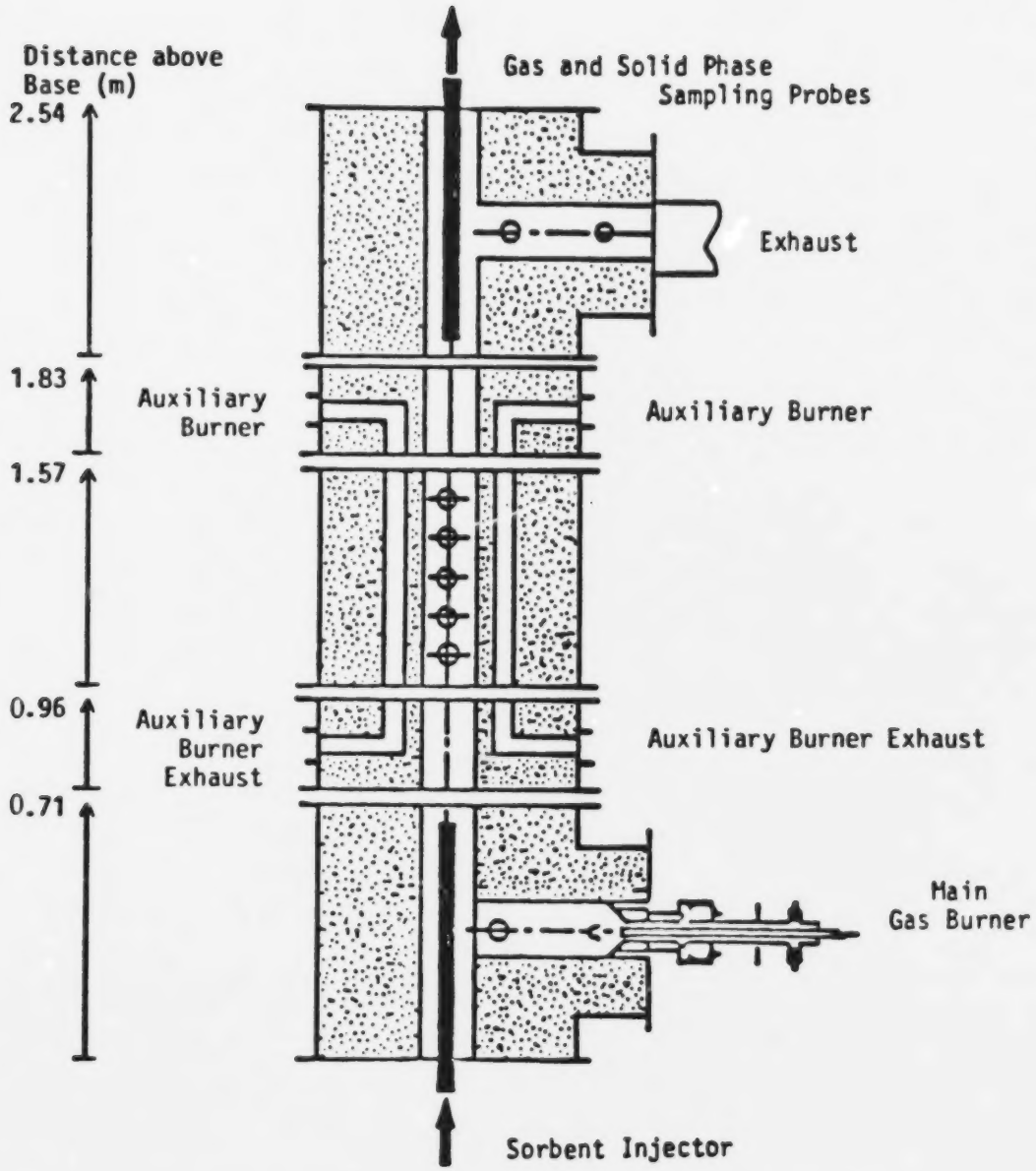

Figure 1. Schematic of Isothermal Reactor

results are also shown in Figure 1. Pure SO_2 was metered into the natural gas prior to the burner to provide the appropriate SO_2 concentration in the reaction zone. The calcium-based sorbents were metered with a calibrated, twin-screw K-tron feeder. The sorbents were transported with nitrogen to a water cooled, showerhead injector located at the bottom of the reaction zone.

Prior to any experimentation, CO, CO_2, and O_2 were measured at both the inlet and the exhaust of the reaction zone to ensure that the fuel species were completely reacted prior to the sulfation zone. SO_2 samples were taken with a temperature-controlled, stainless steel probe which contained a phase-discrimination tip to separate most (> 90%) of the reactive sorbent particles from the primary sample stream. (Radial traverses were conducted to ensure flow uniformity.) After exiting the probe the sample passed through two glass-wool filters to remove any remaining solid material, a heated sample line, two Permapure dryers to remove the moisture, and a 60μm stainless steel final filter. SO_2 concentrations were then measured on a dry basis using a DuPont NDUV 400 photometric analyzer. An overall sulfur balance of > 90% was achieved prior to any experimentation.

Solid samples were also withdrawn at the exit of the reaction zone to characterize the physical properties of the sorbent when

SO_2 was not present. These samples were withdrawn from the furnace using a stainless steel, controlled-temperature probe operated at isokinetic conditions and were collected on a high-temperature filter maintained at 500 K. At the conclusion of the solid sampling sequence, each sample was cooled to room temperature while being purged with dry nitrogen. The samples were then immediately sealed and stored under dry air. Each solid sample was characterized using a Micromeretics model 220 surface area analyzer.

The static calcination experiments were performed with 13 cm quartz "boats" placed in a muffle furnace through which dry nitrogen was passed to remove gas phase calcination products (CO_2 or H_2O). Three gram samples were calcined at 980 K for 20 minutes. The samples were then placed under dry nitrogen and sealed for subsequent surface area analysis. The calcination conditions were selected based on an extensive series of experiments reported previously by Harrison et al.[14] in which surface area and extent of calcination were determined as a function of thermal environment and calcination temperature.

MATHEMATICAL MODELING OF THE SO_2/LIME REACTION

Two basic types of models have been previously applied to the

SO_2/lime reaction system in fluidized bed combustion. Ramachandran and Smith[15], Bhatia and Perlmutter[16], and Simons and Rawlins[17] developed pore models. Pigford and Sligler[18], Hartman and Coughlin[4], and Hartman and Trnka[19] developed grain models. The pore models assume that the calcium oxide particles are spheres containing cylindrical pores which may be of variable size and which either emanate from the surface or are connected in a tree-like structure. The grain models assume porous, spherical CaO particles composed of conglomerates of smaller, non-porous grains of pure CaO. Neither approach appears to perfectly simulate the behavior of flash calcined limestones and hydrates; however, both appear adequate for sulfation modeling.

A grain model was adopted for this study based on high resolution Scanning-Transmission Electron Microscope photographs of calcined dolomite particles which showed a grain-like structure with 100 Å cracks. The modeling of the sulfation reaction by Hartman and Coughlin[4] for fluidized beds was used as a starting point. The calcitic sorbents were assumed to be pure CaO; the dolomitic sorbents were assumed to also form grains of pure MgO. The reaction of the CaO grains with SO_2 was assumed to occur by a shrinking core model. It was also assumed that the final reaction product was $CaSO_4$, that its formation was irreversible, and that

the overall formation could be modeled with the standard, two parameter Arrhenius expression. Because of the differences in the molar volumes of pure CaO and $CaSO_4$ (17 and 46 $cm^3/gmol$), the sulfation reaction necessarily involves the growth of the grains and the concomitant decrease in the porosity of the particle.

The governing differential equations were solved numerically with Newton's method. The solid product-layer diffusion coefficient and intrinsic chemical rate constant were obtained by fitting the conversion versus time data of Borgwardt[5]. Details of the numerical solution and governing equations have been reported previously by Silcox et al.[20].

DISCUSSION OF RESULTS

CALCIUM/SULFUR RATIO

Figure 2 summarizes the results of a series of experiments in which the calcium to sulfur molar ratio was progressively increased while the SO_2 partial pressure was held constant at 2000 ppm and the reactor temperature and residence time were maintained at 1370 K and 500 msec, respectively. Increasing the calcium to sulfur ratio increases the amount of sorbent injected and, hence, the number of available reaction sites. SO_2 capture data (circles) are shown as a function of calcium to sulfur molar ratio

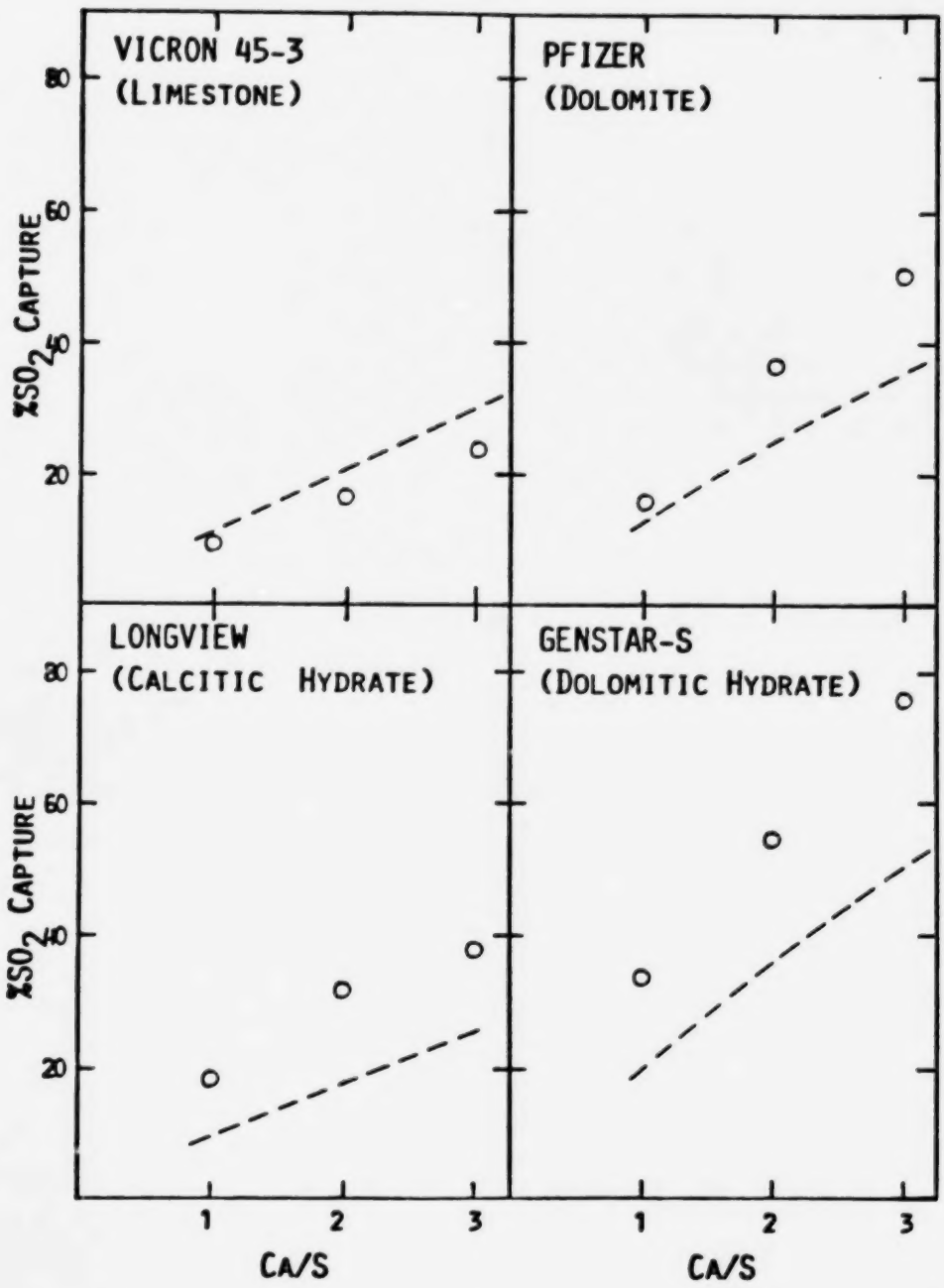

Figure 2. Influence of Ca/S Molar Ratio (Symbols are data @1373 K, 500 msec, and 2000 ppm SO_2; dotted lines are Grain Model predictions).

for sorbents typical of each major sorbent class: a limestone (Vicron 45-3), a dolomite (Pfizer), an atmospheric hydrated calcitic lime (Longview), and a pressure hydrated dolomitic lime (Genstar-S). These data indicate that for all of the sorbents used in this study capture increased approximately linearly with increasing Ca/S ratio suggesting that the overall chemistry is approximately first order in calcium sites. The data also indicate that all of the other sorbents produced higher SO_2 capture than the limestone.

Figure 2 also shows grain model predictions for each of the sorbents studied. These predictions are based on the fundamental rate data of Borgwardt[5] and the measured particle size distribution, surface area, and reactor temperature for each experiment. No parameters were adjusted to improve the agreement between the model predictions and the experimental data. Table 1 shows the physical characteristics of each sorbent which were used as model inputs. The mean particle size was determined based on a sedigraph analysis of the raw sorbent. The surface area was measured by BET analysis of a sorbent sample withdrawn from the furnace at the end of the reaction zone (500 msec) under identical combustion conditions but with no SO_2 present.

TABLE 1

Physical Characteristics of the Sorbents Shown in Figure 2

Sorbent	Mass Mean Diameter (μm)	Surface Area of the Calcined Sorbent (m^2/g)
Vicron limestone	11	14
Pfizer dolomite	34	17.8
Longview calcitic hydrate	4	11.4
Genstar dolomitic hydrate	1.4	25.2

In general the model predictions for the limestone are in good agreement with the measured experimental data; however, the model significantly underpredicts the measured capture for the other sorbents. Table 1 indicates that the dolomitic materials develop correspondingly higher surface areas than the corresponding calcitic sorbents and that in general the hydration process results in a significant decrease in particle size. Both effects served to increase the model predictions, but these changes do not adequately account for the increased capture measured with the other sorbents relative to the limestone. Recent, time resolved surface area data obtained by Slaughter et al.[12] indicate that the surface area actually decreases with increasing residence time in the reactor. Hence, the assumption that calcination is instantaneously

complete and a sorbent can be characterized by a single surface area is probably inadequate, particularly in the case of the more reactive, hydrated materials. Thus, data shown in Figure 2 suggest that to accurately predict the performance of hydrated sorbents in isothermal reactors, the sulfation model must be coupled with a sorbent activation model.

SO_2 PARTIAL PRESSURE

Figure 3 shows the influence of SO_2 partial pressure on gas phase sulfur capture for four typical sorbents at 1370 K, a Ca/S molar ratio of 2.0, and a gas phase residence time of 500 msec. At these conditions no significant dependence of gas phase capture on SO_2 partial pressure was observed for any of the sorbents above a concentration of approximately 1500 ppm SO_2. This is in general agreement with recent pilot scale results[9]; however, the SO_2 dependence observed here is less than the 0.62 power previously reported by Borgwardt[5] for sulfation of 1μm precalcined particles. As the concentration of SO_2 was increased in these experiments, the corresponding concentration of sorbent was also increased proportionately to maintain a constant Ca/S ratio in the combustion gas flow. These data suggest that, at conditions of practical interest for medium to high sulfur Eastern coals, sorbent utilization is almost completely controlled by the availability of

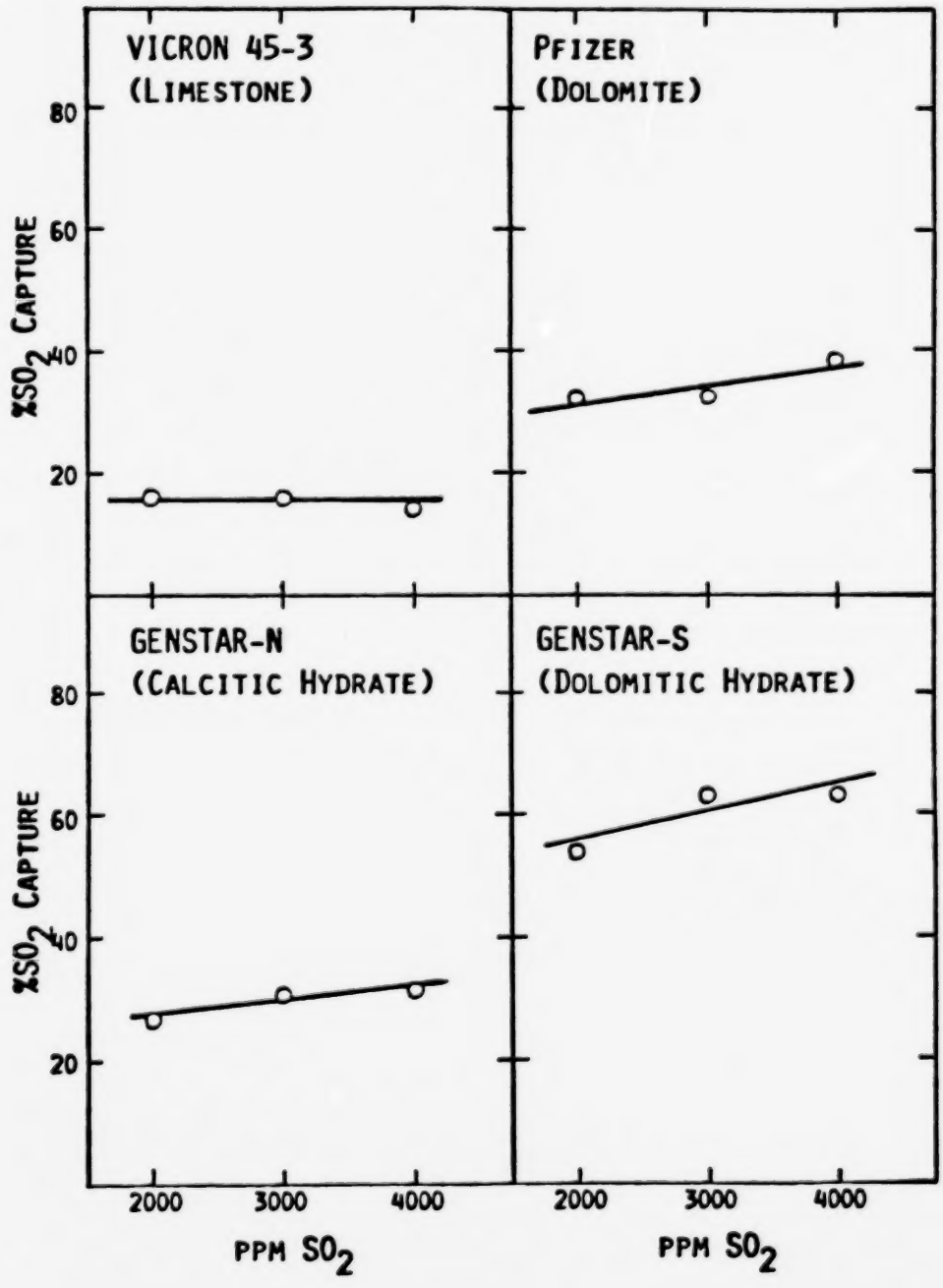

Figure 3. Influence of SO_2 Partial Pressure (1370 K, 500 msec, Ca/S = 2).

calcium sites; the overall reaction rate does not appear to be limited by the transport of SO_2 to the reaction interface.

REACTOR TEMPERATURE

Figure 4 shows the dependence of SO_2 capture on reactor temperature for the four major classes of sorbents. These experiments were conducted with 2000 ppm SO_2, Ca/S molar ratio of 2.0, and a reactor residence time of 500 msec. In general the calcitic materials, Vicron and Longview, and the Pfizer dolomite showed a relatively weak temperature dependence, while the pressure slaked dolomite, Genstar-S, produced optimum SO_2 capture at approximately 1370 K. Interpretation of these data is particularly difficult because of the major, competing processes involved. As the temperature is increased, the calcination process occurs more rapidly but the resultant surface area is smaller due to catalyzed sintering[12]. However this effect is mitigated by increased kinetic and diffusion rates at higher temperatures. Ultimately, at approximately 1500 K, the SO_2 capture is limited by the thermodynamic stability of the calcium sulfate product.

SORBENT COMPARISON

Figure 5 summarizes the SO_2 capture data obtained for all of the sorbents considered in this study at 1370 K, 2000 ppm SO_2,

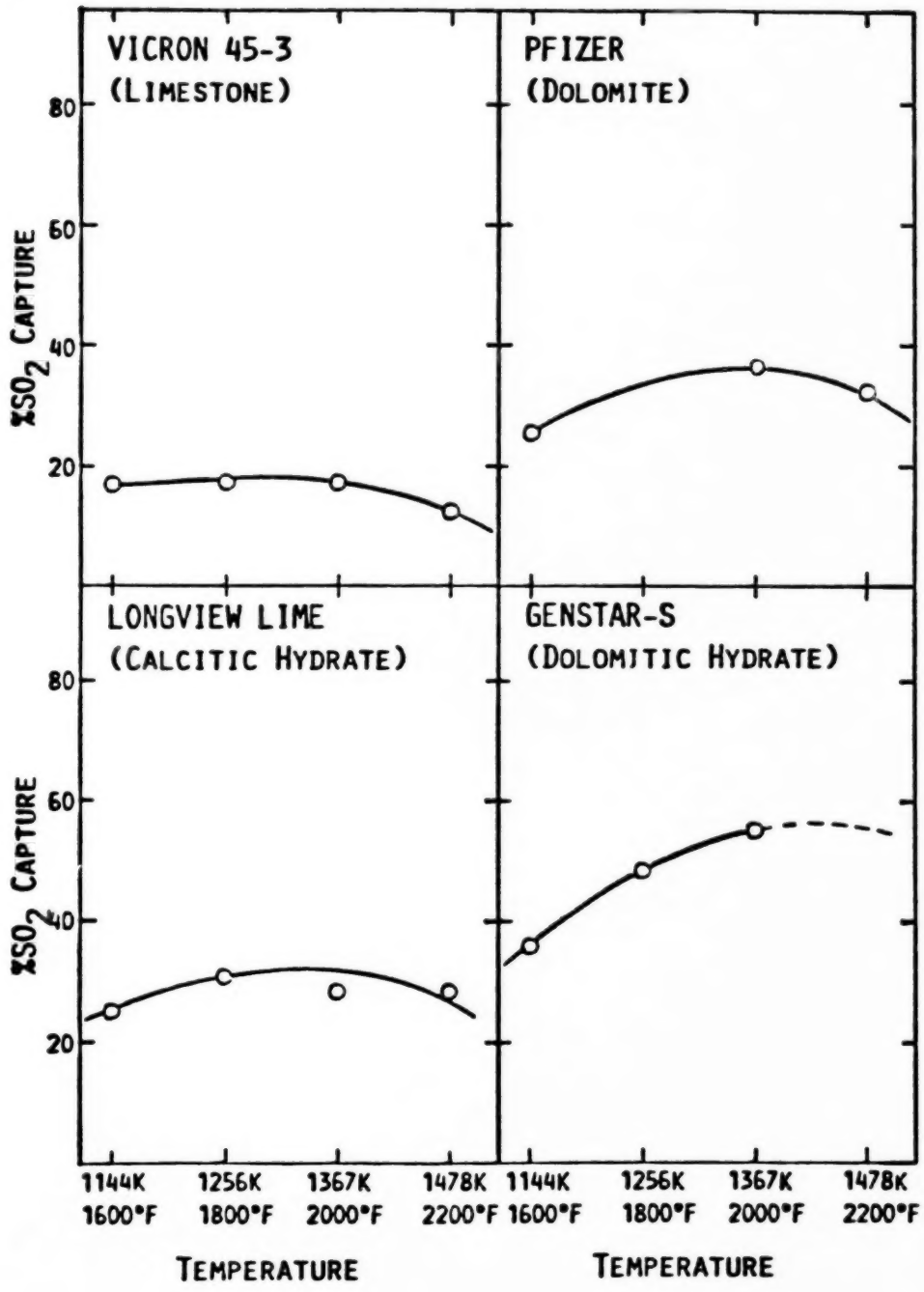

Figure 4. Influence of Reactor Temperature (500 msec, 2000 ppm SO_2, Ca/S = 2).

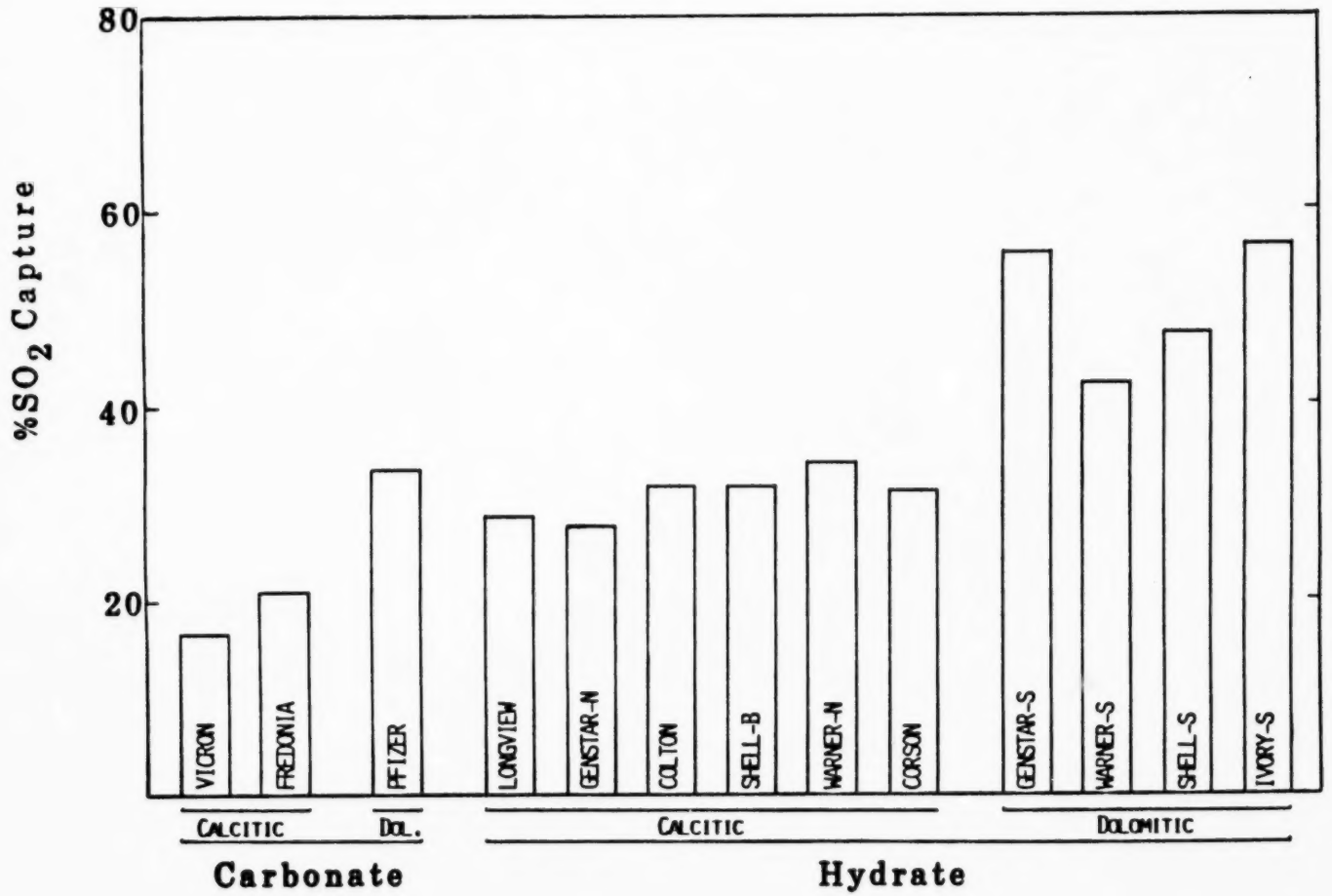

Figure 5. Comparison of Alternative Sorbents: Equivalent Ca Basis (1370 K, 500 msec, 2000 ppm SO_2, Ca/S = 2).

Ca/S = 2.0, and a residence time of 500 msec. These data indicate that in general there are significant differences between capture achieved with each of the four sorbent classes when compared on a equivalent calcium basis. In general the hydrated sorbents, both calcitic and dolomitic, performed better than the raw carbonates, and this finding is in good agreement with recent pilot scale results[9,10,11]. In addition, the dolomitic sorbents, both carbonates and hydrates, produced higher SO_2 capture levels than the corresponding calcitic sorbents.

Figure 5 also indicates that, within each of the four major sorbent classes, the various materials tend to perform approximately equally. Six different hydrated calcitic limes were tested in this study, and the average SO_2 capture was 30 $\pm$ 3%; four pressure hydrated dolomitic limes were evaluated with an average SO_2 capture of 50 $\pm$ 7%. These results suggest that process variations between different commercial manufacturers (especially with atomspheric hydration) do not result in significant differences in reactivity with respect to SO_2 capture.

The superiority of the hydrate sorbents relative to the carbonate sorbents can be attributed to three differences:

- Dehydration occurs significantly more rapidly than CO_2 evolution so that the time available for sulfation after completion of the calcination process is greater with

hydrate sorbents than with carbonate sorbents.

- The dehydration process generally produces a reduction in mean particle size, and this reduces the internal SO_2 diffusion resistence and enhances capture.
- Dehydrated sorbents begin with a much higher initial surface area (ca. $16 m^2/g$ vs $1 m^2/g$).

Figure 6 shows BET surface areas which resulted when the sorbents from Figure 5 were calcined for 20 minutes at 980 K in a static calcination situation surrounded by nitrogen. These conditions were selected based on extensive measurements[14] between 650 and 1250 K. The 980 K results represent an intermediate condition where the hydrates are greater than 90% calcined and the carbonates are approximately 50% calcined. In general the surface areas obtained in this simple calcination experiment mirror the SO_2 capture data obtained in the dispersed phase reactor. The hydrates have larger surface areas than the carbonates and the dolomitic sorbents have larger surface areas than the calcitic sorbents. These data suggest that one of the major differences between the effectiveness of different sorbent classes is the surface area which is produced in the calcination process. It must, however, be noted that the surface areas shown in Figure 6 show significantly larger differences between sorbent classes than

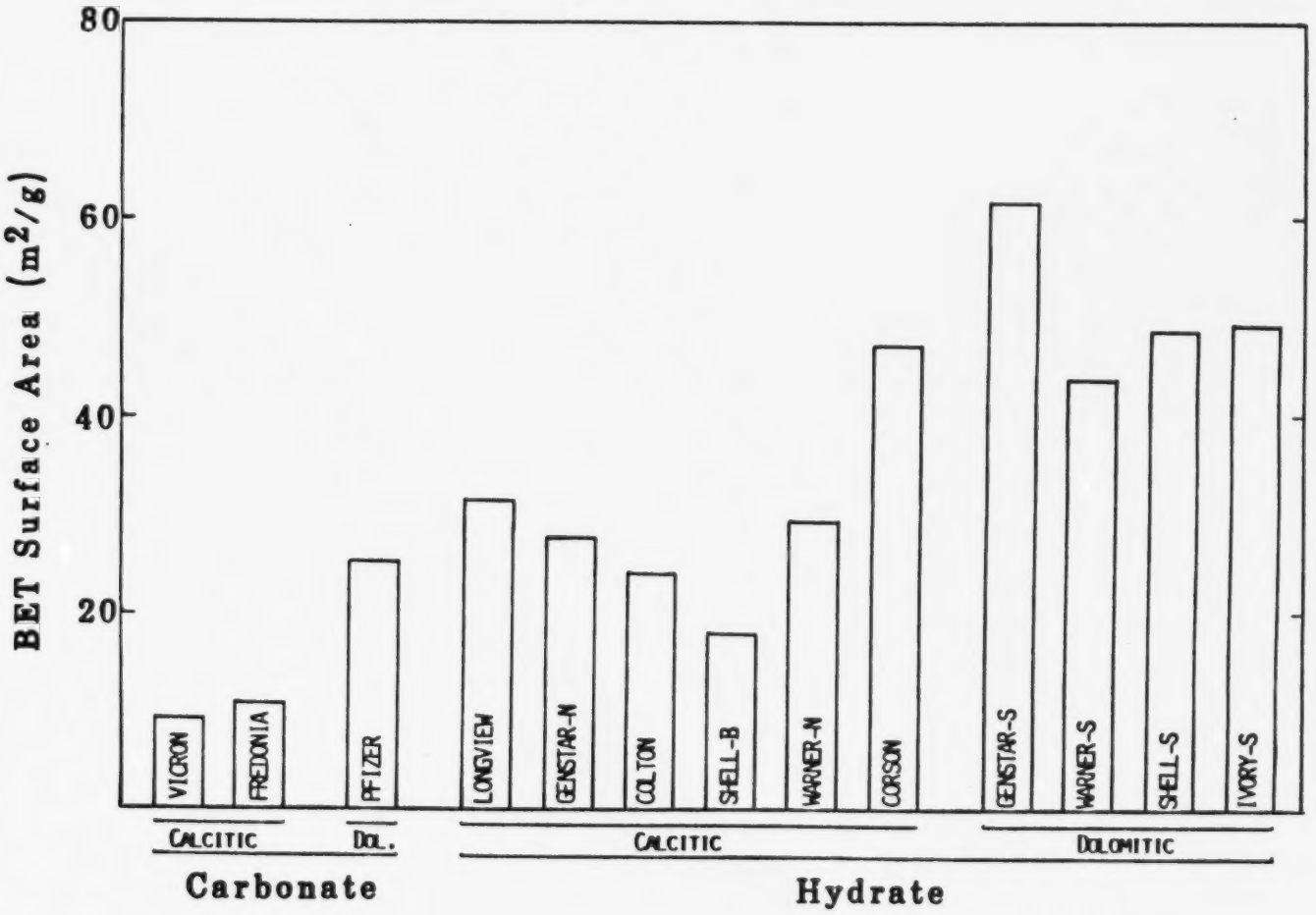

Figure 6. Surface Area Developed During Inert Calcination in Muffle Furnace (980 K, 20 min, 3.0 g sample, N_2 sweep).

those actually measured at the end of the dispersed-phase reactor (see Table 1). The surface area of the hydrated material was approximately equal to that of the carbonate at the end of the dispersed-phase reactor yet the overall capture was much greater with the hydrated sorbent.

Figure 7 shows a direct comparison of the SO_2 capture measurements (dispersed-phase reactor) versus the surface areas from the static calcination experiments (muffle furnace). This figure indicates that the surface areas produced in the simple inert calcination experiment provide a reasonable estimate of sorbent reactivity in an actual sulfation situation.

All of the sorbent comparisons thus far have been made on an equivalent calcium basis because the MgO does not react to form $MgSO_4$ at the thermal conditions of interest here[9]; however, from a practical viewpoint, the mass input with the dolomitic sorbent is significantly greater than that with an equivalent calcitic sorbent. Figure 8 shows the comparative data plotted on a constant mass basis (equivalent to limestone injection at Ca/S ratio = 2.0). These results indicate that on an equivalent mass basis dolomite is essentially equal to limestone and dolomitic hydrates compare directly with atmospheric calcitic hydrates. Thus, from a material handling and cost standpoint, dolomitic materials

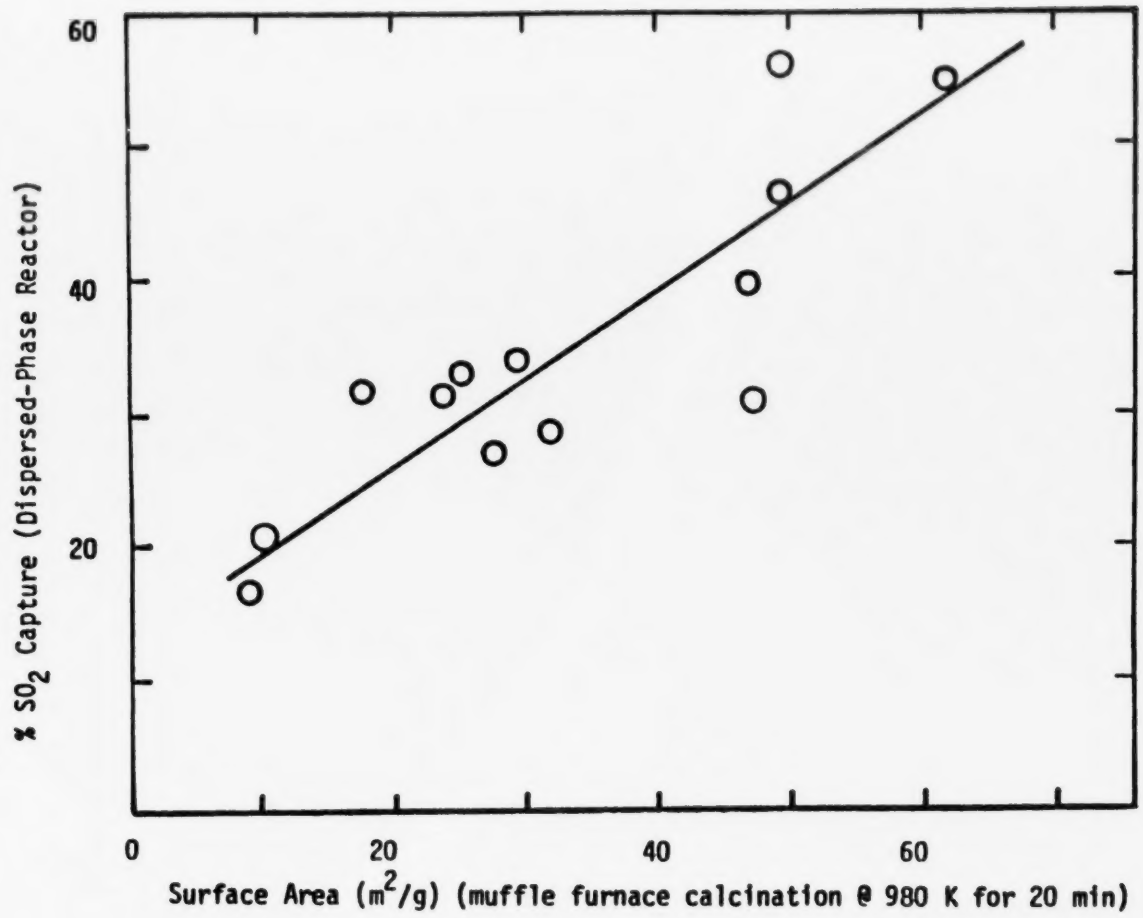

Figure 7. Correlation of SO_2 Capture (Dispersed-Phase Reactor) with Inert Calcination Surface Area (Muffle Furnace). (See Figures 5 & 6 for conditions.)

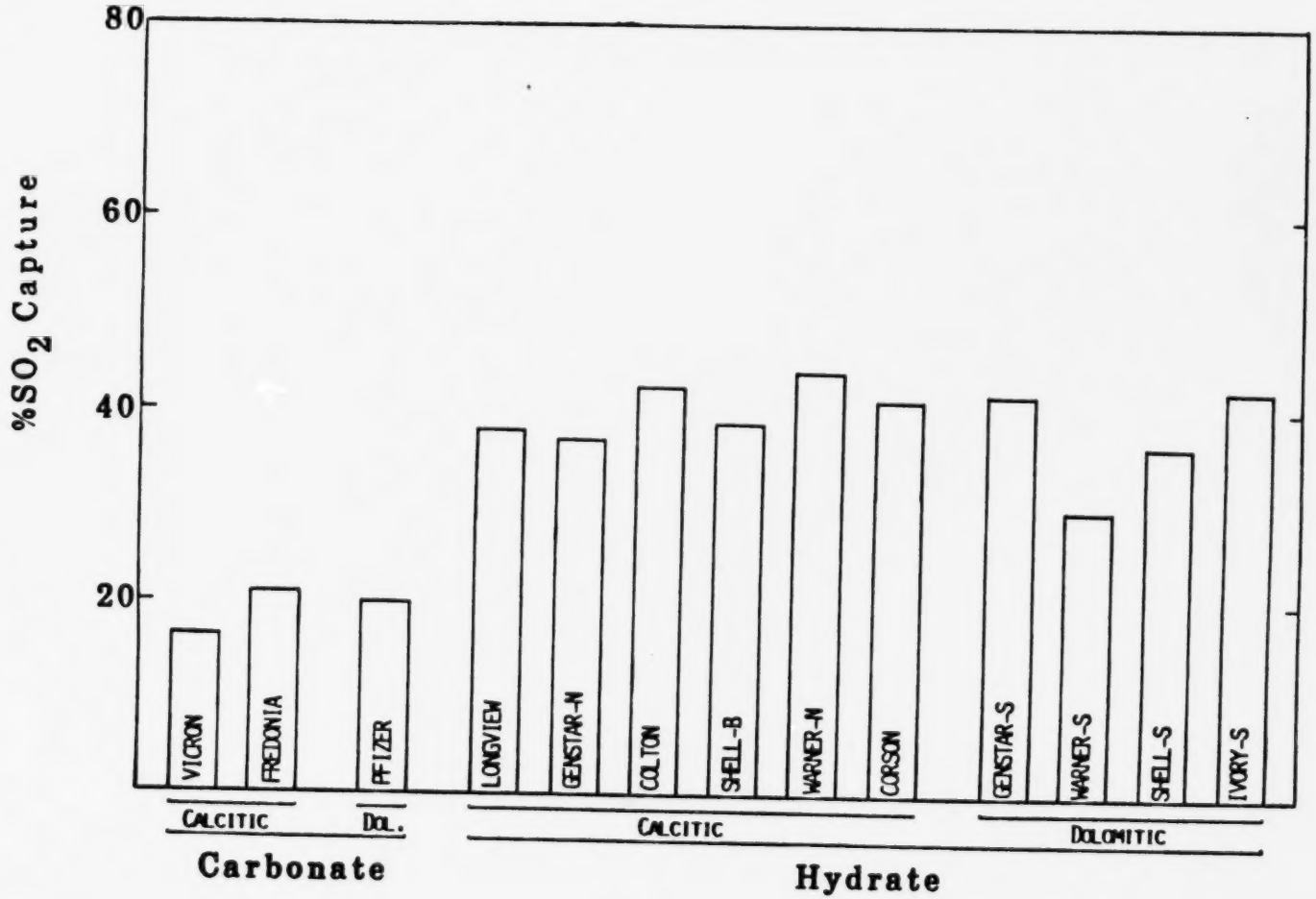

Figure 8. Comparison of Alternative Sorbents: Equivalent Mass Basis (1370 K, 500 msec, 2000 ppm SO_2, Ca/S = 2).

probably do not offer a significant advantage over the calcitic materials.

CONCLUSIONS

This study has shown that the major parameter controlling the degree of SO_2 capture achievable by dry sorbent injection is the type of sorbent used. At a constant Ca/S molar ratio and combustion conditions, hydrated sorbents perform better than carbonated sorbents and dolomitic materials are more active than calcitic materials. Within a particular sorbent class, variations between different commercial products are generally not of first order importance, particularly in the case of atmospheric hydrates. Adsorption of SO_2 is linearly dependent on Ca/S ratio, but relatively insensitive to SO_2 partial pressure above 2000 ppm. Under the isothermal, constant residence time conditions of this study, overall SO_2 capture was found to be only weakly temperature dependent except with the pressure hydrated dolomitic lime.

Sulfation model calculations based on surface areas measured at 500 msec (without SO_2 present) accurately predict capture measured with limestone, but significantly underpredict the performance of other materials.

Calcination studies in an inert atmosphere can be used to

provide an estimate of sorbent reactivity under actual combustion conditions. Sorbents which produce high surface areas under inert calcination conditions generally result in high SO_2 captures.

Because the results of this study were obtained under isothermal conditions, the data are particularly useful for model assessment and validation; however, corresponding results from pilot scale studies with realistic time/temperature profiles are required before any general conclusions regarding boiler injection can be reached.

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